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- Semiconductive ceramic composition.

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SEMICONDUCTIVE CERAMIC COMPOSITION

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BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a semiconductive ceramic composition for a semiconductive ceramic capacitor, and more particularly to a semiconductive ceramic composition suitable for use for manufacturing of a reduction and reoxidation type semiconductive ceramic capacitor.

Description of the Prior Art

A semiconductive ceramic capacitor serving as a passive electronic circuit element is generally classified into two types or a boundary-layer type and a surface-layer type. The boundary-layer type semiconductive ceramic capacitor includes a boundary insulation type one and the surface-layer type semiconductive ceramic capacitor includes a barrier-layer type one and a reduction reoxidation type one.

The semiconductive ceramic capacitor, particularly, reduction reoxidation type semiconductive ceramic capacitor generally has a disadvantage that an increase in unit area capacity expressed at uF/cm² causes a significant decrease in breakdown voltage, resulting in an increase in dielectric loss and/or deterioration of temperature characteristics.

SUMMARY OF THE INVENTION

The present invention has been made in view of the foregoing disadvantage of the prior art.

Accordingly, it is an object of the present invention to provide a semiconductive ceramic composition for a semiconductive ceramic capacitor which is capable of causing the capacitor to exhibit not only increased unit area capacity but increased dielectric strength and excellent temperature characteristics.

It is another object of the present invention to provide a semiconductive ceramic composition for a semiconductive ceramic capacitor which is capable of improving insulation resistance and D.C. breakdown voltage of the capacitor.

It is a further object of the present invention to provide a semiconductive ceramic composition for a reduction reoxidation type semiconductive ceramic capacitor which is capable of causing the capacitor to exhibit not only increased unit area capacity but increased dielectric strength and excellent temperature characteristics.

It is still another object of the present invention to provide a semiconductive ceramic composition for a reduction reoxidation type semiconductive ceramic capacitor which is capable of improving insulation resistance and D.C. breakdown voltage of the capacitor.

In accordance with the present invention, a semiconductive ceramic composition is provided. The composition comprises a BaTiO $_3$ base component and a minor component comprising Nb and Ce. Nb and Ce are present at 0.2 to 3.0 mol% on Nb $_2$ O $_5$ and CeO $_2$ bases, respectively.

In accordance with the present invention, a semiconductive ceramic composition is also provided which comprises a BaTiO₃ base component, a minor component comprising Nb and Ce, and an additive component comprising Co. Mn. SiO2 and SrTiO₃. Nb and Ce are present at 0.2 to 3.0 mol% on Nb₂O₅ and CeO₂ bases, respectively. Co and Mn are present at 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively. SiO₂ and SrTiO3 are present in amounts of 0.25 wt% or less and 0.5 to 20.0 wt%. The additive component may comprise Co, Mn, SiO₂ and CaTiO₃, wherein Co, Mn and SiO2 may be present in the same amounts as described above. CaTiO₃ may be present at 0.2 to 15.0 wt%. Alternatively, the additive component may comprise Co, Mn, SiO2 and Y. Co, Mn and SiO₂ may be present in the same amounts as described above. Y may be present at 0.1 to 3.0 wt% on a Y_2O_3 basis.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a semiconductive ceramic composition for a semiconductive ceramic capacitor, particularly, a reduction reoxidation type semiconductive ceramic capacitor which comprises a BaTiO₃ base component and a minor component comprising Nb and Ce. The term "minor component" used herein indicates an essential component smaller in quantity than the base component. Nb and Ce constituting the minor component are pr s nt in amounts of 0.2 to 3.0 wt% based on Nb₂O₅ and CeO₂ bases, respectively. It was found that use of the composition of such construction for a semiconductive ceramic capaci-

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Use of the so-formulated composition for a semiconductive ceramic capacitor, particularly, a reduction and reoxidation type one likewise causes

the capacitor to be increased in capacity and dielectric strength and exhibit good temperature characteristics.

The composition may further contain Y, which may be present in an amount of 0.1 to 3.0 wt% on a Y₂O₃ basis. Addition of Y causes the capacitor to exhibit improved insulation resistance and D.C. breakdown voltage and more temperature characteristics.

Furthermore, the present invention is directed to a semiconductive ceramic composition for a semiconductive ceramic capacitor, particularly, a reduction reoxidation type semiconductive ceramic capacitor which comprises a BaTiO₃ base component, a minor component comprising Nb and Ce, and an additive component comprising Co, Mn, SiO₂ and Y. Nb and Ce are present in amounts of 0.2 to 3.0 mol% on Nb₂O₅ and CeO₂ bases, respectively. Co and Mn are present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively. SiO₂ is present in an amount of 0.25 wt% or less and Y is present in an amount of 0.1 to 3.0 wt% on a Y2O3 basis. Use of the so-formulated composition for a semiconductive ceramic capacitor, particularly, a reduction and reoxidation type one likewise causes the capacitor to be increased in capacity and dielectric strength and exhibit improved insulation resistance and D.C. breakdown voltage and good temperature characteristics.

Each of the so-formulated semiconductive ceramic composition may be compacted into a semi-conductive ceramic element and sintered to cause a surface layer of the element to be insulated.

The invention will be understood more readily with reference to the following examples, however, these examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

tor, particularly, a reduction and reoxidation type one causes the capacitor to be significantly increased in capacity and dielectric strength and effectively exhibit good temperature characteristics. The composition may also contain Co in an amount of 0.8 wt% or less on a Co₃O₄ basis. Such addition of Co significantly improves insulation resistance and D.C. breakdown voltage of the capacitor and causes it to exhibit more temperature characteristics. Further, the composition may contain Mn in an amount of 0.25 wt% or less on a MnCO₃ basis. In addition, it may contain SiO₂ in an amount of 0.25 wt% or less. Incorporation of Mn and SiO₂ further promotes the above-noted advantage obtained due to addition of Co.

The present invention is also directed to a semiconductive ceramic composition for a semiconductive ceramic capacitor, particularly, a reduction reoxidation type semiconductive ceramic capacitor which comprises a BaTiO₃ base component, a minor component comprising Nb and Ce, and an additive component comprising Co, Mn, SiO₂ and SrTiO₃. Nb and Ce are present in amounts of 0.2 to 3.0 mol% on Nb₂O₅ and CeO₂ bases, respectively. Co and Mn are present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively. SiO₂ and SrTiO₃ are present in amounts of 0.25 wt% or less and 0.5 to 20.0 wt%, respectively.

Use of the so-formulated composition for a semiconductive ceramic capacitor, particularly, a reduction and reoxidation type one likewise causes the capacitor to be substantially increased in capacity and dielectric strength and positively exhibit good temperature characteristics.

The composition may further contain Y, which may be present in an amount of 0.1 to 3.0 wt% on a Y₂O₃ basis. Addition of Y causes the capacitor to exhibit improved insulation resistance and D.C. breakdown voltage and more temperature characteristics.

The present invention is further directed to a semiconductive ceramic composition for a semiconductive ceramic capacitor, particularly, a reduction reoxidation type semiconductive ceramic capacitor which comprises a BaTiO₃ base component, a minor component comprising Nb and Ce, and an additive component comprising Co, Mn, SiO₂ and CaTiO₃. Nb and Ce are present in amounts of 0.2 to 3.0 mol% on Nb₂O₅ and CeO₂ bases, respectively. Co and Mn are present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively. SiO₂ and CaTiO₃ are present in amounts of 0.25 wt% or less and 0.2 to 15.0 wt%, respectively.

Example 1

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BaCO₃, TiO₂, Nb₂O₅, CeO₂, Co₃O₄, MnCO₃ and SiO₂ each having an industrial grade were used as starting materials. The materials were weighed so that each composition may be obtained which has a composition ratio as shown in Table 1. The materials were subjected to wet blending in a ball mill of synthetic resin using water and pebbles for 20 hours while stirring to prepare a composition mixture. Then, the so-obtained mixture was dewatered and dried, and provisionally burned at 1200 °C for 2 hours. Subsequently, the mixture was powdered and blended for 20 hours by means of

the ball mill and then dewatered and dried, to which polyvinyl alcohol (PVA) in an amount of 2 wt% was added as an organic binder to carry out granulation and grading to prepare granulated powder of the composition. The powder was then formed into a disc-like compact or semiconductive ceramic element of 10mm in diameter and 0.5mm in thickness at compacting pressure of about 3 tons/cm2. The element was heat-treated at 800°C for 1 hour to remove the binder therefrom and then subjected to burning at about 1300°C for about 2 hours. Then, it was subjected to reduction at 800°C for 2 hours in a stream of a reducing atmosphere (H₂ atmosphere) to prepare a reduction reoxidation type semiconductive ceramic element, which was then heat-treated at 800°C for 2 hours in an oxidizing atmosphere (air). This caused reoxidation of only a surface of the element, resulting in the surface being provided with an insulating property. Thereafter, an Ag paste was applied onto both surfaces of the semiconductive ceramic element by printing and then baked at 800°C to form electrodes, resulting in a reduction reoxidation type semiconductive ceramic capacitor.

A test was then carried out to consider electrical characteristics of the so-manufactured capacitor. The results were as shown in Table 1, wherein capacity and dielectric loss (tan δ) were measured at a frequency of 1kHz and insulation resistance was measured at a room temperature of 20°C while applying D.C. voltage of 25V to the capacitor.

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	T.C.*6	(8)	+85°C	10	-13	-30	-10	-15	-27	-18	-23	-19	-13	-15	-20	-23
	T	<u> </u>	-25°C	0	+	+8	+3	+3	-1	+ 4	+4	4.	+5	5+	+5	+3
Characteristics	vb*5	(v)		700	200	200	800	700	1000	700	006	700	200	200	200	800
acter	IR*4	(QM)	(103)	0.5	0.7	0.7	2	S	7	2	2		0.7	2	S	ر ک
1	$tan\delta^{*3}$	(%)		10.0	7.0	8.0	4.3	4.0	4.3	3.5	3.7	3.5	11.0	4.3	4.0	3.5
Electrical	c*2	(µF/cm ²)	-	0.02	0.05	0.10	0.15	0.18	0.25	0.27	0.30	0.23	0.05	0.17	0.20	0.21
		\sin_2		0	0	0	O	0	0	0		0	0	0		0
	wt&	MnCO ₃		0	0	0	0	0	0	0	0	0	0	0	0	0
Ratio	•	C0304	,	0	0	0	0	0	0	0	.0	0	0	0 .	0	0
	•	ceo ₂		0.1	0.5	4.0	0.2	0.5	3.0	0.5	1.5	0.5	0.1	0.2	0.5	1.0
Composition	mo18	Nb_2O_5		0.1	0.1	0.1	0.2	0.2	0.2	0.5	0.5	1.0	1.5	1.5	1.5	1.5
		\mathtt{BaTiO}_3		8.66	99.4	95.9	9.66	99.3	8.96	0.66	0.86	98.5	98.4	98.3	0.86	97.5
	Spec- imen	No.		H	7 .	ю	4	Ŋ	9	7	ω	σ	10	11	1.2	13
	1			×	×	×							×			

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Table 1 (Continued)

	9*:		+85°C	-25	-28	-30	-40	-22	-26	-20	-23	-30	-25	-30	-45	-25
	T.C	%	-25°C	+1	0	ا ش	-10	+3	+4	+5	+ 5	-2	+13	+7	0	-15
Characteristics	vb*5	(\$		200	800	1000	1000	700	800	700	200	800	300	300	300	700
acter	IR*4	(MD)	(103)	ر ک	വ	Ŋ	2	2	2	ស	2	2	0.5	0.7	0.5	2
	$tan\delta^{*3}$	(%)		3.7	3.8	4.0	7.0	4.0	4.0	4.0	4.5	4.3	12.0	8.0	8.0	4.2
Electrical	C*2	(µF/cm ²)		0.23	0.25	0.26	0.28	0.20	0.23	0.15	0.15	0.20	0.05	.200	0.05	0.24
		sio ₂		0	0	0	0	0	0	. 0	0	0	0	0	0	. 0
	wt&	MnCO ₃		0	0	0	0	0	0	0	. 0	0	0	0	0	0
Ratio	-	Co304	-	0	0	0	0	Ö	0	0	0	0	0	0	0	0.03
1 1		ceo ₂		1.5	2.0	3.0	4.0	0.5	1.5	0.2	0.5	3.0	0.1	0.5	4.0	0.5
Composition	mo18	Nb ₂ 0 ₅		1.5	1.5	1.5	1.5	2.0	2.0	3.0	3.0	3.0	4.0	4.0	4.0	1.5
		\mathtt{BaTio}_3		97.0	96.5	95.5	94.5	97.5	96.5	8.96	96.5	94.0	95.9	95.5	92.0	98.0
	Spec- imen	o		14	15	16	17	18	19	20	21	22	23	24	25	26
	⊣						×						×	×	×	

Table 1 (Continued)

			Composition	ition R	Ratio			Electrical	1	racter	Characteristics		
imen mol%	mol%	mo18	l		-	wt&		c*2	$tan \delta^{*3}$	IR*4	Vb*5	T.C	c. *6
No. Bario ₃ Nb ₂ O ₅	Nb ₂ 0	Nb ₂ 0 ₅	1	ceo ₂	Co304	MnCO ₃	Si02	(µF/cm ²)		(MD)	(\(\)	8)	
									·	(10^3)		-25°C	+85°C
27 98.0 1.5	.0 1.	•		0.5	0.05	0	0	0.23	4.0	Ŋ	700	-10	27
28 98.0 1.5	.0 1.	•		0.5	0.10		0	0.20	4.0	2	700	0	-23
29 98.0 1.5	.0 1.	•		0.5	0.20	0	0	0.20	4.0	S	200	+5	-20
30 98.0 1.5	.0 1.	•		0.5	0.50	0	0	0.18	3.5	2	700	+5	-16
31 98.0 1.5	8.0 1.	•		0.5	0.80	0	0	0.14	3.5	S	1000	9+	-14
32 98.0 1.5	.0 1.	•		0.5	1.00	0	0	0.04	3.0	S	1000	+5	-10
33 98.0 1.5	.0 1.	•		0.5	0.20	0.003	0	0.15	4.0	7	006	+3	-20
34 98.0 1.5	.0 1.	•		0.5	0.20	0.005	0	0.20	3.6	10	1100	+5	-20
35 98.0 1.5	.0 1.	•		0.5	0.20	0.03	0	0.18	3.5	20	1500	+4	-20
36 98.0 1.5	.0 1.	•		0.5	0.20	0.05	0	0.20	3.5	20	1500	+5	-20
37 98.0 1.5	.0 1.			0.5	0.20	0.10	0	0.20	3.3	20	1500	+5	-20
38 98.0 1.5	.0 1.	•		0.5	0.20	0.15	0	0.15	3.3	20	1300	+3	-20
39 98.0 1.5	.0 1.	•	ŀ	0.5	0.20	0.25	0	0.14	3.0	10	1000	+4	-18

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As can be seen from Table 1, specimen Nos. 1, 2, 3, 10, 17, 23, 24, 25, 32, 40 and 44 are not included in the scope of the invention. More particularly, Table 1 indicates that Nb2O5 in an amount below 0.2 mol% or exceeding 3.0 mol% causes the capacitor to be decreased in unit area capacity C and increased in dielectric loss tan as well as decreased in insulation resistance IR and D.C. breakdown voltage Vb (Specimen Nos. 1, 2, 3, 23, 24 and 25). Also, it indicates that CeO2 below 0.2 mol% causes the capacitor to be decreased in capacity and increased in dielectric loss; whereas when the amount of CeO2 is above 3.0 mol%, the capacitor is increased in dielectric loss and exhibits improper temperature characteristics (Specimen Nos. 1, 3, 10, 17, 23 and 25). Co₃O₄ in an amount above 0.8 wt% and MnCO3 above 0.25 wt% caused the capacity to be decreased (Specimen No. 32) and the D.C. breakdown voltage to be decreased (Specimen No. 40), respectively. Further, SiO₂ exceeding 0.25 wt% led to a decrease in capacity, insulation resistance and D.C. breakdown voltage of the capacitor (Specimen No. 44).

Thus, it will be noted that the semiconductive ceramic composition of the present invention effectively exhibits the above-noted advantages.

Example 2

Example 1 was substantially repeated except that BaCO₃, TiO₂, Nb₂O₅, CeO₂, Co₃O₄ MnCO₃, SiO₂ SrCO₃ and Y₂O₃ in such amounts as shown in Table 2 were used as starting materials. The results were as shown in Table 2.

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Table 2

Г			Τ	l			-					_				
	T.C.*6	8	+85°C	-10	-13	-30	-10	-15	-27	-18	-13	-15	-20	-25	-30	-40
	H		-25°C	, 0	+1	+8	+3	+3	-	+4	+5	+5	+ 5	+1	r I	-10
tics	4P*5	(>)		700	500	200	800	700	1000	700	200	700	700	700	1000	1000
Characteristics	IR*4	(MD)	(10 ³)	0.5	0.7	0.7	2	<u>ب</u>	7	ഗ	0.7	رح د	Z.	ر.	2	5
1	$tan \delta^{*3}$	(%)		10.0	7.0	8.0	4.3	4.0	4.3	3.5	11.0	4.3	4.0	3.7	4.0	7.0
Electrical	c*2	(µF/cm ²)		0.02	0.05	0.10	0.15	0.18	0.25	0.27	0.05	0.17	0.20	0.23	0.26	0.28
H		3 Y ₂ O ₃		0	0	0	0	0	0	0	o .	0	0	0	0	0
		SrTio		0	0	0	0	0	0	0	0	0	0		0	0
	wt&	Sio2		0	0	0	0	0	0	0	. 0	0	0	0	0	. 0
io	-	MnCO ₃		0	, 0	0	0	0	0	0	0	0	0	0	0	0
on Ratio	•	C0304		0	0	0	0	0	0	0	0	0	0	0	0	0
Composition	dР	CeO ₂		0.1	0.5	4.0	0.2	0.5	3.0	0.5	0.1	0.2	0.5	1.5	3.0	4.0
Сощр	mol8	Nb205		0.1	0.1	0.1	0.2	0.2	0.2	0.5	1.5	1.5	1.5	1.5	1.5	1.5
		$BaTiO_3$		99.8	99.4	95.9	9.66	99.3	8.96	0.66	98.4	98.3	98.0	97.0	95.5	94.5
_	imen	No.		н	2	ю	4	S	9	7	80	6	10	11	12	13
*	·			×	×	×					×				·	×

Table 2 (Continued)

;			Comp	Composition	on Ratio	0				Electrical	Characteristics	teris	tics		
- ↓. k	Spec- imen	,	mo18	ф	•		wt&			c*2	tan 6 ^{*3}	IR*4	vb*5	T.C	c.*6
	ON	BaTiO ₃	Nb205	CeO ₂	C0304	MnCO ₃	Sio ₂ s	SrTio	3 Y ₂ 0 ₃	$(\mu F/cm^2)$	(%)	(MD)	(2)		&·)
												(10^3)		-25°C	+85°C
	14	8.96	3.0	0.2	0	0	0	0	0	0.15	4.0	Ŋ	700	+ 5	-20
	15	96.5	3.0	0.5	0		0	0	0	0.15	4.5	Ŋ	200	15 +	-23
	16	94.0	3.0	3.0	0	0	0	0	0	0.20	4.3	2	800	-2.	-30
*	17	95.9	4.0	0.1	0	0	0	0	0 .	0.05	12.0	0.5	300	+13	-25
×	18	. 95.5	4.0	0.5	0	0	0	0	0	0.07	8.0	0.7	300	+7	-30
×	19	92.0	4.0	4.0	0	0	0		0	0.05	8.0	0.5	300	0	-45
	20	98.0	1.5	0.5	0.03	0	0	0	0	0.24	4.2	S	200	-15	-25
	21 .	0.86	1.5	0.5	0.10	. 0	0	0	0 .	0.20	4.0	2	100	.0	-23
	22	0.86	1.5	0.5	0.20	0	0	0	0	0.20	4.0	5	200	+ 5	-20
	23	0.86	1.5	0.5	08.0	0	0	0	0	0.14	3.5	2	1000	9+	-14
×	24	0.86	1.5	0.5	1.00	0	0	0	0	0.04	3.0	Ŋ	1000	+5	-10
	25	0.86	1.5	0.5	0.20	0.05	. 0	0	0	0.20	3.5	20	1500	+5	-20
	26	98.0	1.5	0.5	0.20	0.25	0	0	. 0	0.14	3.0	10	1000	+4	-18

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Table 2 (Continued)

*	Coco		Сошр	Composition	on Ratio	0) = 1	Electrical	ŀ	Characteristics	tics		
4 -	imen		mo1%	96	•	<u>-</u>	wt&			c*2	$tan \delta^{*3}$	IR*4	vb*5	H.	T.C.*6
	No.	BaTiO ₃	Nb ₂ 0 ₅	CeO	C0304	MnCO ₃	Sio2	SrTio3	Y203	(µF/cm ²)		_	(v)		8
												(103)		-25°C	+85°C
×	27	98.0	1.5	0.5	0.20	0.35	0	0	0	0.18	2.0	S	300	+5	-15
	28	98.0	1.5	0.5	0.20	0.05	0.05	0	0	0.20	3.6	20	1500	+5	-20
	29	98.0	1.5	0.5	0.20	0.05	0.25	0	0	0.14	4.0	10	1000	+3	-18
×	30	98.0	1.5	0.5	0.20	0.05	0.35	0	0	0.05	5.0	H	200	+3	-15
×	31	98.0	1.5	0.5	0.20	0.05	0.05	0.2	0	0.20	3.4	20	1500	+5	-20
	32	98.0	1.5	0.5	0.20	0.05	0.05	0.5	0	0.19	2.5	20	1800	+5	-21
	33	98.0	1.5	0.5	0.20	0.05	0.05	5.0	0	0.17	2.5	10	1500	& + ·	-23
	34	0.86	1.5	0.5	0.20	0.05	0.05	10.0	0	0.14	2.3	10	1200	+10	-26
	35	98.0	1.5	0.5	0.20	0.05	0.05	20.0	0	0.14	2.2	S	850	+15	-30
×	36	98.0	1.5	0.5	0.20	0.05	0.05	30.0	. 0	0.35	2.0	0.2	350	-10	-65
×	37	98.0	1.5	0.5	0.20	0.05	0.05	20.0	0	0.14	2.2	S	850	+15	-30
×	38	98.0	1.5	0.5	0.20	0.05	0.05	0	0.05	0.20	3.5	20	1500	+5	-21
×	39	0.86	1.5	0.5	0.20	0.05	0.05	0	3.0	0.16	3.3	10	2000	+5	-20

Table 2 (Continued)

Ratio wt8 304 MnCO ₃ SiO ₂ SrTiO ₃	Composition Ratio mol8 Nb ₂ 0 ₅ Ce0 ₂ Co ₃ 0 ₄ MnCO ₃ Si0 ₂ SrTi0 ₃	Composition Ratio mol% wt% Nb ₂ 0 ₅ Ce0 ₂ Co ₃ 0 ₄ MnCO ₃ Si0 ₂ SrTi0 ₃	Section Ratio wt 8 CeO ₂ Co ₃ O ₄ MnCO ₃ SiO ₂ SrTiO ₃	Ratio wt8	wt% SiO ₂ SrTiO ₃			Y203	Electrical c^{*2} $(\mu F/cm^2)$	tan5*3 IR*4 vb*5 (MC) (v)	teri IR*4 (MD)	stics vb*5 (v)	T. C	.c. *6	
	T										(103)		-25°C	+85°C	- 1
40		98.0	1.5	0.5	0.20 0.05	0.05	0.2	0.1	0.20	3.5	20	1800	+5	-20	
41		98.0	1.5	0.5	0.20 0.05	0.05	0.5	0.1	0.20	2.5	20	2000	+5	-20	
4.2		98.0	1.5	0.5	0.20 0.05	0.05	20.0	0.1	0.18	2.1	8	1400	+10	-26	
43		0.86	1.5	0.5	0.20 0.05	0.05	30.0	0.1	0.37	2.2	0.7	200	-7	09-	
44		98.0	1.5	0.5	0.20 0.05	0.05	0.2	3.0	0.18	3.5	20	1800	+5	-20	
45		98.0	1.5	0.5	0.20 0.05	0.05	0.5	3.0	0.18	2.3	20	2000	+3	-21	
46		0.86	1.5	0.5	0.20 0.05	0.05	20.02	3.0	0.15	2.1	10	1500	+12	-29	
47		98.0	1.5	0.5	0.20 0.05	0.05	30.0	3.0	0.38	2.1	9.0	700	1.5	-62	
4.8		0.86	1.5	0.5	0.20 0.05	0.05	0.5	4.0	0.05	7.4	10	1600	9+	-15	
49		98.0	1.5	0.5	0.20 0.05	0.05	30.0	4.0	0.29	4.2	0.5	009	-7	-58	

X indicates specimens which are not included in the scope of the present invention. *1:

*2: C indicates unit area capacity

lable 3

_																
	T.C.*6	(&)	⊃•58÷	. – 10	-13	-30	-10	-15	-27	-18	-13	-15	-20	-25	-30	-40
	H		-25°C	0	+	+	+3	+3	Ţ	+4	+5	+5	+5	+1+	۳ <u>-</u>	- 10
tics	۸p*5	3		700	200	200	800	700	1000	700	200	700	700	700	1000	1000
Characteristics	IR*4	ŒW)	(103)	0.5	0.7	0.7	Ŋ	ß	7	, s	0.7	S	2	S.	2	Ŋ
1 1	tan6*3	(8)		10.0	7.0	8.0	4.3	4.0	4.3	3.5	11.0	4.3	4.0	3.7	4.0	7.0
Electrical	C*2	(µF/cm ²)		0.02	0.05	0.10	0.15	0.18	0.25	0.27	0.05	0.17	0.20	0.23	0.26	0.28
14		3 Y ₂ 03		0	0	0	0	0	0	0	0	0	0	0	0	0
		$cario_3$		0	0	0	0	0	0	0	0	0	0	0	0	0
	wt&	\sin_2		0	0	0	0	0	0	0	0	0	0	0	0	0
io	•	Mnco ₃		0	0	0	0	0	0		0	0	0	0	0	0
on Ratio	•	Co304		0	0	0	0	0	0	0	0			0	0	0
Composition	ф	CeO ₂		0.1	0.5	4.0	0.2	0.5	3.0	0.5	0.1	0.2	0.5	1.5	3.0	4.0
Сошр	mo18	Nb205		0.1	0.1	0.1	0.2	0.2	0.2	0.5	1.5	1.5	1.5	1.5	1.5	1.5
		BaTiO3		8.66	99.4	95.9	9.66	99.3	8.96	0.66	98.4	98.3	98.0	97.0	95.5	94.5
	spec- imen	No.		н	7	e	4	ស	9	7	cc	6	10	11	12	13
				×	×	×					×				· ·	×

Table 3 (Continued)

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										-						
	T.C. *6	\$	+85°C	, -15	-20	-18	-15	-20	-17	-15	-5	+3	+82	+3	-21	-20
	T.	·	-25°C	+5	+5	+3	+3	+5	+1	۳-	-15	-22	-27	-22	+5	+5
stics	۸p*5	?		300	1500	1000	200	1500	1900	2000	1800	1500	1100	1500	1500	2000
cteri	1R*4	Ø₩)	(103)	വ	20	10	7	20	20	20	10	7	ر ک	7	20	10
Characteristics	$tan \delta^{*3}$	(%)		2.0	3.6	4.0	5.0	3.6	3.6	3.8	4.0	4.5	8.0	4.5	3.5	3.3
Electrical	c*2	(µF/cm ²)		0.18	0.20	0.14	0.05	0.20	0.22	0.25	0.23	0.20	0.05	0.20	0.20	0.16
		x ₂ 0 ₃		0	0	o	0	0	0	0	0	0	0	0	0.05	3.0
		caTio ₃		0	0	0	0	0.1	0.2	2.0	10.0	15.0	20.0	15.0	0	0
	wt&	sio_2		0	0.05	0.25	0.35	0.05	0.05	0,05	0.05	0.05	0.05	0.05	0.05	0.05
0.1	-	Mnco ₃		0.35	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
on Rati		co304		0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Composition	de.	ceo2		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Comp	mo18	Nb ₂ 0 ₅		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
		BaTiO3		98.0	0.86	0.86	0.86	0.86	98.0	98.0	98.0	0.86	0.86	0.86	98.0	98.0
	Spec- imen	No.		27	28	29	30	31	32	33	34	35	36	37	38	39.
!				×			×	×					×	×	×	×

BEST AVAILABLE COPY (Continued indicates temperature characteristics ന **Table** breakdqwn voltage insulation resistance D.C. indicates Vb indicates IR

Further, CaTiO₃ less than 0.2 wt% failed in a significant increase in capacity and D.C. breakdown voltage of the capacitor, whereas when CaTiO3 exceeds 15.0 wt%, the capacitor was decreased in capacity, increased in dielectric loss and exhibited improper temperature characteristics (Specimen Nos. 31, 36, 42 and 46).

Furthermore, Table 3 indicates that Y2O3 in an amount below 0.1 wt% fails in a significant increase of D.C. breakdown voltage of the capacitor and Y2O3 above 3.0 wt% decreases the capacity (Specimen Nos. 31, 37, 38, 39, 43, 47 and 48).

Thus, it will be noted that the semiconductive ceramic composition of the present invention effectively exhibits the above-noted advantages.

Example 4

Example 1 was substantially repeated except that BaCO₃, TiO₂, Nb₂O₅, CeO₂, Co₃O₄ MnCO₃, SiO₂ and Y2O3 in such amounts as shown in Table 4 were used as starting materials. The results were as shown in Table 4.

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Table 3 indicates that Nb₂O₅ in an amount below 0.2 mol% or exceeding 3.0 mol% causes the capacitor to be decreased in unit area capacity C and increased in dielectric loss $\tan \delta$, as well as decreased in insulation resistance IR and D.C. breakdown voltage Vb (Specimen Nos. 1, 2, 3, 17, 18 and 19). Also, it indicates that CeO2 below 0.2 mol% causes the capacitor to be decreased in capacity and increased in dielectric loss; whereas when the amount of CeO2 is above 3.0 mol%, the capacitor is increased in dielectric loss and exhibits improper temperature characteristics (Specimen Nos. 1, 3, 8, 13, 17 and 19). Co₃O₄ in an amount above 0.8 wt% and MnCO3 above 0.25 wt% caused the capacity to be decreased (Specimen No. 24) and the D.C. breakdown voltage to be decreased (Specimen No. 27), respectively. Further, SiO₂ exceeding 0.25 wt% resulted in a decrease in capacity, insulation resistance and D.C. breakdown voltage of the capacitor (Specimen No. 30).

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Table 4 (Continued)

		<u>/:\</u>	· -				·		mg i .		· <u>-</u> ,	Ψ,			-		7	:-
, 9	BILE			39					0 2	256 4	05					40		
BEST AVAILA			T.C. *6	(8)	+85°C	20	-23	-30	-25	-30	-45	-25	-23	-20	-14	-10	-20	-18
*					-25°C	+5	+5	-2	+13	+7	. 0	-15	0	+5	9+	+5	+5	+
•	•	tics	Vb*5	(>		100	200	800	300	300	300	700	004	700	1000	1000	1500	1000
		Characteristics	IR*4		(10 ³)	മ	Ŋ	2	0.5	0.7	0.5	2	Ŋ	رد .	ιΩ	Ŋ	20	10
		. !	tan 6*3	(&)		4.0	4.5	4.3	12.0	8.0	8.0	4.2	4.0	4.0	3.5	3.0	3.5	3.0
	ed)	Electrical	c*2	(µF/cm ²)		0.15	0.15	0.20	0.05	0.07	0.05	0.24	0.20	0.20	0.14	0.04	0.20	0.14
	(Continued)			Y203		0	0	0	0	0	0	0	0	0	0	0	0.	0
	4			sio ₂		0	Ο.	0	0	0	0	0	0	0	0	0	. 0	0
	Table		wt 8	MnCO ₃		. 0	0	0	. 0	0	0	0	0	0	0	0	0.05	0.25
		Ratio	-	Co304		0	0	0	0	0	0	0.03	0.10	0.20	0.80	1.00	0.20	0.20
				ceo2		0.2	0.5	3.0	0.1	0.5	4.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
		Composition	mol8	Nb205		3.0	3.0	3.0	4.0	4.0	4.0	1.5	1.5	1.5	1.5	1.5	1.5	1.5
				BaTiO ₃		96.8	96.5	94.0	95.9	95.5	92.0	98.0	98.0	0.86	98.0	0.86	0.86	98.0
· ·			spec- imen	No.		14	15	16	17	18	19	20	21	22	23	24	25	26
			-	·	\perp				×	<u>×_</u>	×_					×		

Table 4 (Continued)

į	100		Composition	ition	Ratio				Electrical	1 Characteristics	cteris	tics		
	Spec- imen		mol&		-	wt&			c*2	tan6*3	IR*4	vb*5		T.C.*6
	0	BaTiO ₃	Nb_2O_5	CeO ₂	C0304	$^{\mathrm{MnCO_3}}$ $^{\mathrm{SiO_2}}$ $^{\mathrm{Y_2O_3}}$	\sin_2	x ₂ 0 ₃	(µF/cm ²)	(&)	(MD)	(^)		(%)
											(103)		-25°C	+85°C
	27	98.0	1.5	0.5	0.20	0.35	0	0	0.18	2.0	2	300	+5	-15
	28	98.0	1.5	0.5	0.20	0.05	0.05	0	0.20	3.6	20	1500	+5	-20
	29	98.0	1.5	0.5	0.20	0.05	0.25	0	0.14	4.0	10	1000	+3	-18
	30	98.0	1.5	0.5	0.20	0.05	0.35	0	0.05	5.0	H	200	+3	-15
	31	0.86	1.5	0.5	0.20	0.05	0.05	0.05	0.20	3.5	20	1500	+5	-21
	32	0.86	1.5	0.5	0.20	0.05	0.05	0.10	0.23	3.5	20	2000	+5	-20
	33	98.0	1.5	0.5	0.20	0.05	0.05	1.0	0.21	3.2	20	2000	+3	-23
	34	98.0	1.5	0.5	0.20	0.05	0.05	3.0	0.16	3.3	10	2000	+5	-20
	35	98.0	1.5	0.5	0.20	0.05	0.05	4.0	0.03	8.2	10	2000	+10	-10

X indicates specimens which are not included in the scope of the present invention.

*3: tan δ indicates dielectric loss.

^{2:} C indicates unit area capacity.

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Table 4 (Continued)

*5: Vb indicates D.C. breakdown voltage *6: T.C. indicates temperature characteristics

Table 4 indicates that Nb₂O₅ in an amount below 0.2 mol% or exceeding 3.0 mol% causes the capacitor to be decreased in unit area capacity C and increased in dielectric loss $tan \delta$, as well as decreased in insulation resistance IR and D.C. breakdown voltage Vb (Specimen Nos. 1, 2, 3, 17, 18 and 19). Also, it indicates that CeO2 below 0.2 mol% causes the capacitor to be decreased in capacity and increased in dielectric loss; whereas when the amount of CeO₂ is above 3.0 mol%, the capacitor is increased in dielectric loss and exhibits improper temperature characteristics (Specimen Nos. 1, 3, 8, 13, 17 and 19). Co₃O₄ in an amount above 0.8 wt% and MnCO3 above 0.25 wt% caused the capacity to be decreased (Specimen No. 24) and the D.C. breakdown voltage to be decreased (Specimen No. 27). Further, SiO₂ exceeding 0.25 wt% led to a decrease in capacity, insulation resistance and D.C. breakdown voltage of the capacitor (Specimen No. 30).

Furthermore, Table 4 indicates that Y_2O_3 in an amount below 0.1 wt% fails in a significant increase of D.C. breakdown voltage of the capacitor and Y_2O_3 above 3.0 wt% decreases the capacity and increases the dielectric loss (Specimen Nos. 31 and 35).

Thus, it will be noted that the semiconductive ceramic composition of the present invention effectively exhibits the above-noted advantages.

While the invention has been described with a certain degree of particularity with reference to the examples, obvious modifications and variations are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

 A semiconductive ceramic composition comprising:

a base component comprising BaTiO₃; and a minor component comprising Nb and Ce; said Nb and Ce being present in amounts of 0.2 to 3.0 mol% on Nb₂O₅ and CeO₂ bases, respectively.

- 2. A semiconductive ceramic composition as defined in Claim 1 further comprising Co, said Co being present in an amount of 0.8 wt% or less on a Co₃O₄ basis.
- 3. A semiconductive ceramic composition as defined in Claim 2 further comprising Mn, said Mn being present in an amount of 0.25 wt% or less on a MnCO₃ basis.
- 4. A semiconductive ceramic composition as defined in Claim 3 further comprising SiO_2 , said SiO_2 being present in an amount of 0.25 wt% or less.
- 5. A semiconductive ceramic composition as defined in Claim 1 further comprising an additive component comprising Co, Mn, SiO_2 and $SrTiO_3$, said Co and Mn being present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co_3O_4 and $MnCO_3$ bases, respectively, and said SiO_2 and $SrTiO_3$ being present in amounts of 0.25 wt% or less and 0.5 to 20.0 wt%, respectively.
- 6. A semiconductive ceramic composition as defined in Claim 5 further comprising Y, said Y being present in an amount of 0.1 to 3.0 wt% on a Y_2O_3 basis.
- 7. A semiconductive ceramic composition as defined in Claim 1 further comprising an additive component comprising Co, Mn, SiO_2 and $CaTiO_3$, said Co and Mn being present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co_3O_4 and

IR indicates insulation resistance.

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Table 3 (Continued)

			Сошр	ositic	Composition Ratio	0				g	Chara	eri	tics.		
spec- imen			mo18	dρ	•		wt&			C*2	an δ^{*3}	.R*4	v _b *5	E .	T.C.*6
No. Ba	B	aTiO3	Bario ₃ Nb ₂ O ₅ CeO ₂	CeO ₂	Co304	MnC0 ₃	sio_2	Sio ₂ CaTiO ₃ Y ₂ O ₃	^x 2 ⁰ 3	(µF/cm ²)	(8)	(GM)	(^)		(%)
												(103)		-25°C	+85°C
40		0.86	1.5	0.5	0.20	0.05	0.05	0.2	0.1	0.22	3.5	20	2000	+3	-18
41		98.0	1.5	0.5	0.20	0.05	0.05	15.0	0.1	0.22	3.7	10	1900	-15	+5
42		0.86	1.5	0.5	0.20	0.05	0.05	20.0	0.1	0.08	6.3	7	1600	-24	+91
4.3	_	98.0	1.5	0.5	0.20	0.05	0.05	0.1	3.0	0.16	3.3	10	1700	+5	-21
44		98.0	1.5	0.5	0.20	0.05	0.05	0.2	3.0	0.20	3,3	20	2000	+3	-19
45		98.0	1.5	0.5	0.20	0.05	0.05	15.0	3.0	0.20	4.4	10	1800	-20	+2
46		98.0	1.5	0.5	0.20	0.05	0.05	20.0	3.0	0.07	7.1	7	1400	-27	+95
47		98.0	1.5	0.5	0.20	0.05	0.05	0:2	4.0	90.0	5.2	10	2000	+5	-18
X · 48		98.0	1.5	0.5	0.20	0.05	0.05	15.0	4.0	0.05	4.8	7	1700	-18	-1

X indicates specimens which are not included in the scope of the invention.

^{*2:} C indicates capacity per unit area

^{*3:} tan δ indicates dielectric loss.

Table 3 (Continued)

1 29ec		Τ			····												
Specific Composition Ratio Richard Characteristics Specific Composition Ratio Composition Comp	cteristics		(8	ညိ	20	-23	-30	-25		4	-25	-23	-20	-14	-10	-20	-18
Speck		F		25°		+5	-2	+13	+7	0	~	0	.+5	9+	+5	+5	+4
Spec-		vb*5			700	200	800	300	300	300	700	700	700	1000	1000	1500	1000
Spec-		IR	(MD)	(10^3)	ഗ	S	Ŋ	•	0.7	•	S	2	S	ς.	Ŋ	20	10
Spec-	i	tan 8*3			4.0	•	•	7	•	8.0	•	•	•	•	3.0	•	
Spec- mol	Electrical		(µF/cm ²)		0.15	0.15	0.20	0.05	0.07	0.05	•	0.20	0.20	. 1	0.04	•	•
No. BaTiO ₃ Nb ₂ O ₅ CeO ₂ Co ₃ O ₄ MnCO ₃ SiO ₂ 14 96.8 3.0 0.2 0 0 0 0 15 96.5 3.0 0.5 0 0 0 16 94.0 3.0 3.0 0 0 0 17 95.9 4.0 0.1 0 0 0 18 95.5 4.0 0.1 0 0 0 20 98.0 1.5 0.5 0.20 0 21 98.0 1.5 0.5 0.80 0 22 98.0 1.5 0.5 0.80 0 24 98.0 1.5 0.5 0.20 0 25 98.0 1.5 0.5 0.20 0 26 98.0 1.5 0.5 0.20 0 27 98.0 1.5 0.5 0.80 0 28 98.0 1.5 0.5 0.20 0.5 0			>-		0	0	0	0	0	0	0	0	0	0	0	0	0
No. BaTiO ₃ Nb ₂ O ₅ CeO ₂ Co ₃ O ₄ MnCO ₃ S 14 96.8 3.0 0.2 0 0 0 15 96.5 3.0 0.5 0 0 0 16 94.0 3.0 3.0 0 0 17 95.9 4.0 0.1 0 0 0 18 95.5 4.0 0.5 0 0 19 92.0 4.0 4.0 0 20 98.0 1.5 0.5 0.20 0 21 98.0 1.5 0.5 0.20 0 22 98.0 1.5 0.5 0.20 0 23 98.0 1.5 0.5 0.20 0 24 98.0 1.5 0.5 0.20 0.05 25 98.0 1.5 0.5 0.20 0.05			CaTio		0	0	0	0	0	0	0	0	0	0	0	0	0
Spec- imen		wt &	Sio		. 0	0	0	o .	0	0	0	0	, 0	0	0	0	0
Tomposition mole mole mole mole mole mole coordinates with mole co	io		MnCO ₃		0		0	0	0	0	0	,0	0	0	0	•	•
No. BaTiO ₃ N 14 96.8 15 96.5 16 94.0 17 95.9 18 95.9 19 95.9 20 98.0 21 98.0 22 98.0 23 98.0 24 98.0 25 98.0	1 1		Co30		0	0	0	0	0	0	Ú.03	0.10	0.20	0.80	1.00	0.20	0.20
No. BaTiO ₃ N 14 96.8 15 96.5 16 94.0 17 95.9 18 95.9 19 95.9 20 98.0 21 98.0 22 98.0 23 98.0 24 98.0 25 98.0	Compositio	8 P	Ce02		0.2	0.5	3.0	0.1	0.5	4.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
11 Spec- imen No. 14 15 16 17 18 19 20 21 22 23 24 24 25		mol	Nb ₂ 0 ₅		3.0	3.0	3.0	4.0	4.0	4.0	•	1.5	•	•	•	1.5	•
			BaTiO ₃		•	•	94.0	•	•	92.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0
	Code	imen	ON		14	15	16	17	18	19	20	21	2.2	23	24	25	26
								×	×	×							

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(Continued) Table

characteristics breakdown voltage resistance dielectric loss insulation indicates indicates indicates tan S S 9

temperature indicates T.C.

Table 2 indicates that Nb₂O₅ in an amount below 0.2 mo% or exceeding 3.0 mol% causes the capacitor to be decreased in unit area capacity C and increased in dielectric loss tan δ , as well as decreased in insulation resistance IR and D.C. breakdown voltage Vb (Specimen Nos. 1, 2, 3, 17, 18 and 19). Also, it indicates that CeO2 below 0.2 mol% causes the capacitor to be decreased in capacity and increased in dielectric loss; whereas when the amount of CeO2 is above 3.0 mol%, the capacitor is increased in dielectric loss and exhibits improper temperature characteristics (Specimen Nos. 1, 3, 8, 13, 17 and 19). Co₃O₄ in an amount above 0.8 wt% and MnCO3 above 0.25 wt% caused the capacity to be decreased (Specimen No. 24) and the D.C. breakdown voltage to be decreased (Specimen No. 27). Further, SiO2 exceeding 0.25 wt% led to a decrease in capacity, insulation resistance and D.C. breakdown voltage of the capacitor (Specimen No. 30).

Further, SrTiO3 less than 0.5 wt% failed in a significant decrease in dielectric loss of the capacitor, whereas when SrTiO3 exceeds 20.0 wt%, the capacitor failed to exhibit good temperature characteristics and was decreased in insulation resistance and D.C. breakdown voltage (Specimen Nos. 31, 36, 38, 39, 40, 43, 44, 47 and 49).

.Furthermore, Table 2 indicates that Y2O3 in an amount below 0.1 wt% decreases D.C. breakdown voltage of the capacitor and Y2O3 above 3.0 wt% decreases the capacity (Specimen Nos. 37 and

Thus, it will be noted that the semiconductive ceramic composition of the present invention effectively exhibits the above-noted advantages.

Example 3

Example 1 was substantially repeated except that BaCO₃, TiO₂, Nb₂O₅ CeO₂, Co₃O₄, MnCO₃, SiO₂, CaCO3 and Y2O3 in such amounts as shown in Table 3 were used as starting materials. The results were as shown in Table 3.

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EUROPEAN SEARCH REPORT

Application number

	DOCUMENTS CONSI	DERED TO BE RELEVANT		EP 87111158.9
Category		indication, where appropriate, int passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Х	JP - A - 61-99 2	207 (ASAHI CHEMICAL IND KK)	1	C 04 B 35/46 H 01 B 1/08
х	<u>JP - A - 57-208</u> * Totality *	OO3 (KYORITSU YOUGYO GEN)	1,2	
X	<u>JP - A - 57-128</u> * Totality *	903 (MATSUSHITA ELEC IND KK)	1,3-9, 11-13	
				TECHNICAL FIELDS SEARCHED (Int. Cl.4)
				C 04 B H 01 B
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	The present search report has be Place of search	1	Examiner	
	VIENNA	Date of completion of the search 18-11-1987	1	BECK

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document

PO Form 1503 03 62

T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

MnCO $_3$ bases, respectively, and said SiO $_2$ and CaTiO $_3$ being present in amounts of 0.25 wt% or less and 0.2 to 15.0 wt%, respectively.

- 8. A semiconductive ceramic composition as defined in Claim 7 further comprising Y, said Y being present in an amount of 0.1 to 3.0 wt% on a Y₂O₃ basis.
- 9. A semiconductive ceramic composition as defined in Claim 2 further comprising an additive component comprising Co, Mn, SiO₂ and Y, said Co, Mn and Y being present in amounts of 0.8 wt% or less, 0.25 wt% or less and 0.1 to 3.0 wt% on Co₃O₄, MnCO₃ and Y₂O₃ bases, respectively, and said SiO₂ being present in an amount of 0.25 wt% or less.
- 10. A semiconductive ceramic composition as defined in any one of Claims 1 to 9, wherein said composition is compacted and sintered to cause a surface layer thereof to be insulated.
- 11. A semiconductive ceramic composition comprising:

a base component comprising BaTiO₃;

a minor component comprising Nb and Ce, said Nb and Ce being present in amounts of 0.2 to 3.0 mol% on Nb₂O₃ and CeO₂ bases, respectively; and

an additive component comprising Co, Mn, SiO₂ and SrTiO₃, said Co and Mn being present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively, and said SiO₂ and SrTiO₃ being present in amounts of 0.25 wt% or less and 0.5 to 20.0 wt%, respectively.

12. A semiconductive ceramic composition comprising:

a base component comprising BaTiO3;

a minor component comprising Nb and Ce, said Nb and Ce being present in amounts of 0.2 to 3.0 mol% on Nb₂O₃ and CeO₂ bases, respectively; and

an additive component comprising Co, Mn, SiO₂ and CaTiO₃, said Co and Mn being present in amounts of 0.8 wt% or less and 0.25 wt% or less on Co₃O₄ and MnCO₃ bases, respectively, and said SiO₂ and CaTiO₃ being present in amounts of 0.25 wt% or less and 0.2 to 15.0 wt%, respectively.

A semiconductive ceramic composition comprising:

a base component comprising BaTiO3;

a minor component comprising Nb and Ce, said Nb and Ce being present in amounts of 0.2 to 3.0 mol% on Nb₂O₃ and CeO₂ bases, respectively; and

an additive component comprising Co, Mn, SiO₂ and Y, said Co, Mn and Y being present in amounts of 0.8 wt% or less, 0.25 wt% or less and 0.1 to 3.0 wt% on Co₃O₄, MnCO₃ and Y₂O₃ bases, respectively, and said SiO₂ being present in an amount of 0.25 wt% or less.

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